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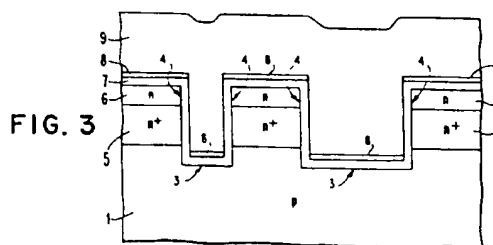
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(54) **Method of filling trenches in semiconductor substrates with silicon.**

(57) A relatively deep trench let into a surface of a semiconductor substrate is filled with silicon to provide a void-free isolation region by covering the semiconductor surface into which the trench is let and the base (3) and/or the side walls (4) of the trench with non-nucleating material (7), providing a layer of nucleating material (8) on at least a portion of the surface of the non-nucleating material and growing silicon (9) perpendicularly from the base or sidewalls of the trench.



METHOD OF FILLING TRENCHES IN
SEMICONDUCTOR SUBSTRATES WITH SILICON

This invention relates to a method of filling trenches in semiconductor substrates with polycrystalline silicon or epitaxial silicon or both. The method of the present invention is particularly applicable to the filling of trenches employed for device isolation purposes.

It has been suggested to form relatively deep trenches in semiconductor substrates and then to refill the trenches in order to provide isolation between active regions or devices in the substrate. For instance, deep trenches can be formed according to the procedures disclosed in U.S.-A-4,256,514. The refill techniques employed in deep trench formations have been chemical vapor deposition (CVD) systems. Such systems involve a homogeneous gas phase reaction. The silicon dioxide or polycrystalline silicon formed in the gas from the reactive gas species present, essentially "drops" onto surfaces and into the trench structures. However, that process suffers from a serious reliability problem in that there is a tendency to form large voids within the trench. In fact, frequently voids are formed at the bottom of the trenches and/or large continuous openings are formed extending to the final surface after subsequent planarization. Moreover, the refill deposited by such procedure can be structurally deficient (e.g., loosely packed) which can lead to problems in future processing. The presence of voids has a tendency to magnify the formation of defects in silicon areas later to serve as active or device regions. This is particularly so if the formation continues up to the surface followed by subsequent oxidation or isolation. Moreover, substrate surfaces which are relatively densely populated with trenches in some areas and less densely populated in others have been found to display local deposition thickness variations. This is due to depletion effects arising from the

presence of increased area. These overall surface variations can cause problems in later planarization steps.

The present invention makes it possible to significantly reduce, if not entirely eliminate, the problem of void formation in isolation trenches experience by prior techniques.

The present invention provides a method of filling a trench let into a surface of a semiconductor substrate with silicon, comprising the steps of: covering the semiconductor surface into which the trench is let and the base and/or the side walls of the trench with non-nucleating material, providing a layer of nucleating material on at least a portion of the surface of the non-nucleating material and growing silicon perpendicularly from the base or sidewalls of the trench.

How the invention can be carried out will now be described by way of example, with reference to the accompanying drawings, in which:-

Figures 1-6 are cross-sectional views of a substrate at successive stages of processing demonstrating the basic method of the present invention; and

Figures 7-13 are cross-sectional views of representative substrates containing a nucleating layer on various alternative surfaces suitable for carrying out the present invention.

For convenience, the discussion of the process steps is directed to employing a P-type silicon substrate as the semiconductor substrate and N-type impurities as the dopant impurities. Of course, as an

alternative, an N-type substrate and P-type dopant impurities can be employed. References to horizontal and/or vertical surfaces or walls are relative to the major surfaces of the substrate.

When the discussion refers to N-type impurities, the process steps are applicable to P-type impurities and vice versa. Also, the present invention is applicable to substrates other than silicon. Moreover, the terms "polysilicon" and polycrystalline silicon are used herein interchangeably as in the prior art.

Referring to figure 1, there is shown a fragment of a semiconductor substrate 1 having trenches 2 therein. The substrate 1 can be a P-type silicon substrate having any desired crystal orientation (e.g. $\langle 100 \rangle$). Such a substrate can be prepared by slicing and polishing a P-type silicon boule grown in the presence of a P-type dopant, such as boron, following conventional crystal growth techniques. Other P-type dopants for silicon include aluminium, gallium, and indium.

Each of the deep trenches 2 has a substantially horizontal surface 3 and substantially vertical surfaces 4. Generally, the surfaces 4 are vertical or less than about 5° from the vertical. The trenches can be formed by the process disclosed in U.S.-A-4,256,514. Generally, the ratio of the depth of the trench to the width of the trench is between about 3.5 to 1 and 2.5 to 1. Of course, larger ratios such as about 4 to 1 are within the scope of the present invention. Typically, the depth of the trench is about 3.5 to 4 microns and the width is about 1 to 2.5 microns.

Adjacent the lower portion of the trenches 2 are n^+ regions 5 and adjacent the upper portion of the trenches are n regions 6. Such regions are desirably formed by ion implantation or thermal diffusion either before or after the formation of the trenches 2.

A non-nucleating layer 7, such as silicon dioxide, silicon nitride, aluminium oxide, or mixtures thereof, is grown on at least one of the surfaces within trench 2 such as on the vertical surfaces 4 within trench 2. For convenience, layer 7 is also grown along the horizontal surface 3 of trench 2. The non-nucleating layer is a relatively thin layer about 0.2 nm to about 0.5 nm thick and typically about 0.3 nm thick. The non-nucleating layer can be provided by any well-known method, such as by thermal oxidation. In addition, the thickness of the non-nucleating layer on surface 3 need not be the same as the thickness of the non-nucleating layer on surfaces 4. Preferably the non-nucleating layer 7 is provided on at least one of the surfaces located along the longest axis of the trench. In the structure shown in figure 1, the longest axis is along the vertical walls 4 of the trench.

Next, a layer 8 of nucleating material is formed on at least one of the surfaces of the non-nucleating layer 7 as shown in figure 2. Typically, this layer is about 500 to about 3000 angstroms thick. It has been noted that if the nucleating layer is too thin, or less than about 500 angstroms, then back etching can occur during the filling technique which thereby causes void formation and decreased speed in the filling technique. The nucleating layer can be deposited by either atmospheric or a low pressure CVD technique to provide polycrystalline silicon. It is preferred that the relatively thin nucleating layer be deposited by low temperature techniques, using temperatures up to about 650°C. Figure 2 illustrates a preferred configuration wherein the nucleating layer 8 is present only on the horizontal surface 3 of the trench and on the horizontal surfaces of the non-nucleating layer on top of the silicon substrate.

Other configurations of the nucleating layer within the scope of the present invention are shown in figures 7 through 13. For instance, figure 7 shows the nucleating layer 8 on top of the non-nucleating material 7 on the horizontal surface of the substrate located outside trench 2. The bottom 3 of trench 2 is exposed silicon which also acts

as a nucleating material. Non-nucleating material 7 is present on the vertical walls of the trench. Figure 8 illustrates covering the non-nucleating material 7 on the vertical walls 4 of the trench and the horizontal layer outside the trench with a nucleating layer. The horizontal surface 3 of trench 2 is exposed substrate 1. Figure 9 illustrates providing nucleating material 8 on the non-nucleating material 7 on the vertical sidewalls 4 of trench 2. The horizontal bottom portion 3 of trench 2 is exposed silicon. Figure 10 illustrates providing a nucleating layer 8 on all surfaces above non-nucleating material 7. Figure 11 illustrates providing a nucleating layer 8 over all of the surfaces of trench 2 wherein the horizontal surface 3 of trench 2 is exposed silicon substrate and the vertical surfaces 4 of trench 2 are non-nucleating material 7. The techniques illustrated in figures 8-11 are not particularly preferred since small amounts of voids have been noted in their formation.

Accordingly, it is preferred that the nucleating material within the trench be present on either only the vertical surfaces 4 or only on the horizontal surface 3.

Figure 12 illustrates providing a non-nucleating material layer 7 on the horizontal surface of trench 2 and on the horizontal surfaces located outside trench 2. The nucleating layer 8 is provided over all surfaces of the trench (ie vertical walls 4, horizontal surface 3) and on the horizontal surface above the non-nucleating layer 7 on the substrate located outside trench 2.

The present invention is also applicable to filling trenches which are located substantially parallel to or at any angle to the top surface of the substrate in addition to the trenches shown which are substantially perpendicular to the top surface of the substrate. For example, figure 13 illustrates a structure wherein the trench is about 90° from that shown in figure 12. In particular, figure 13 illustrates providing a non-nucleating material layer 7 on the vertical surface of

the trench 2. The nucleating layer 8 is provided over all surfaces of the trench and on the vertical surfaces outside the trench. The preferred nucleating layer is polycrystalline silicon.

Next, silicon 9 is grown in trench 2 and on all surfaces containing the nucleating material. The preferred method of growing the silicon according to the present invention is by a gas-solid or heterogeneous reaction system. In particular, the growth occurs perpendicularly from the nucleated surfaces. The heterogeneous reaction system desirably includes hydrogen, silicon, and chlorine. A particularly preferred system is a combination of $\text{SiCl}_4\text{-H}_2$ as discussed by Silvestri and Tang - Reproducible Technique for Simultaneous Deposition of Poly-Epi on Oxide-Silicon, IBM Technical Disclosure Bulletin, Volume 23, No 2, July 1980, pages 819 and 820.

The problem addressed by the present invention of preventing void formation in deep trenches was not encountered in the process discussed by Silvestri and Tang in their publication because the latter is not concerned with deep trench filling.

The filling process is generally carried out at temperatures between about 900 and about 1100°C and preferably about 1000°C to provide a sufficiently fast filling of the trenches. It is important that the filling of the trenches is completed in about 20 minutes or less so that the dopant impurities already present in the substrate are not disturbed due to the exposure to elevated temperatures. With the typical dimensions discussed hereinabove, the filling rate to provide a practical process is at least about 0.22 microns per minute.

In addition to the ability to achieve a void-free fill, the technique employed also improves the planarity of the surfaces as discussed in the aforementioned IBM Technical Disclosure Bulletin.

The type of silicon fill that will be present within the trenches will depend upon the type of nucleating surface present. For instance, polycrystalline nucleating surfaces will result in the formation of polycrystalline silicon. On the other hand, silicon nucleating surfaces, such as shown in figures 7, 8, and 9 will result in epitaxial silicon growth. Accordingly, as illustrated in figures 7, 8, and 9 there will be a combination of polycrystalline silicon 9A and epitaxial silicon 9B.

It has been noted that the silicon in the above types of systems grow faster within holes than on adjacent flat surfaces on single crystal surfaces. Along these lines, see Runyan et al, Journal Electro-Chemical Society, Behavior of Large-Scale Surface Perturbations During Silicon Epitaxial Growth, November 1967, pages 1154-1157. This phenomenon may be due to the existence of higher temperatures at the bottom of the hole and the lack of carrier gas flow in the holes. In addition, in view of the fact that the growth in the trench is faster than on the adjacent flat surfaces, the surface topology is improved.

Next, the silicon layer 9 is planarized for example by a technique discussed in U.S.-A-4,256,514 employing either Cl/argon or CBrF_3 . However, the preferred technique comprises providing a relatively thick layer of resist material 10 over the grown silicon surfaces as illustrated in figure 4. The photoresist material can be applied by well-known techniques such as spinning on or by spraying. The photoresist material tends to flow and provide a substantially level surface as indicated in figure 4. The particular photoresist material employed for this purpose is not critical and any type, negative or positive, of photoresist material can be employed. This is possible since the subsequent steps, as will be discussed hereinbelow, are not dependent upon the chemical identity of the photoresist material. Examples of suitable photoresist materials include compositions based on phenolformaldehyde novalak polymers. A particular example of such is Shipley 1350 which is an m-cresol formaldehyde novalak polymer

composition. This is a positive resist composition and includes therein a diazoketone, such as 2-diazo-1-naphthol-5-sulphonic acid ester. The composition usually contains about 15% by weight of the diazoketone compound. In addition, in other systems, the diazoketone is attached directly to the polymer molecules. A discussion of photoresist materials can be found, for instance, in Journal of the Electrochemical Society, Vol 125, No 3, March 1980 - Deckert et al, "Micro-lithography - Key to Solid-State Fabrication", pp 45C to 56C. The photoresist is generally applied in a thickness of about 2 to about 4 microns.

Next, the structure is subjected to reactive ion etching. The apparatus disclosed in Ephrath, IEEE Transactions on Electron Devices, Reactive Ion Etching for VLSI, Vol, ED-28, No 11, November 1981, p 1315 to 1319 and Ephrath, Semiconductor Silicon 1981, The Electrochemical Society, Dry Etching for VLSI-A Review pp 627 to 637, can be employed for this purpose.

The reactive ion etching procedure employs conditions such that polycrystalline silicon and/or epitaxial silicon etches at the same rate as the photoresist material and at a rate substantially higher than silicon dioxide. The relative amount of the reactive gases, in particular CF_4 and O_2 , and the pressure and the rf power to the two electrodes are adjusted such that the etch rate of the photoresist material is about equal to that of the epitaxial silicon. A particularly preferred system contains about 20% by volume of O_2 at a pressure of about 100 millitorr (13.3 N/m^2). The rf power density to the substrate electrode is 0.27 W/cm^2 and the rf power density to the substrate electrode is 0.1 W/cm^2 . The flow rate of the etching gas is about 40 SCCM and the temperature of the wafer is between 60 and 100°C . Under these conditions, the etch rate of silicon and photoresist is about 60 nm/min and the etch rate of SiO_2 is 7.0 nm/min . Thus, etching stops at the oxide surface 7.

If desired, as illustrated in figure 5, the silicon is etched a small distance inside the trench 2, such as about 200 nm.

Next, the particular devices can be fabricated on and in the substrate. For instance, as an example, the surfaces of the remaining polycrystalline silicon 9 in the trench can be doped to provide an n^+ region, for example by being doped with POCl_3 . If desired, the polycrystalline silicon can now be oxidized to provide isolation regions 11 on top of the n^+ regions. It is noted that the polycrystalline silicon, since it is heavily doped, is oxidized about 4 times as fast as oxidation growth on the epitaxial silicon at a temperature of about 800°C . Accordingly, subsequent to the oxide growth, the oxide can be etched to leave oxide remaining on the polycrystalline silicon, but exposing the epitaxial silicon region.

CLAIMS

1. A method of filling a trench let into a surface of a semiconductor substrate with silicon, comprising the steps of covering the semiconductor surface into which the trench is let and the base and/or the side walls of the trench with non-nucleating material, providing a layer of nucleating material on at least a portion of the surface of the non-nucleating material and growing silicon perpendicularly from the base or sidewalls of the trench.
2. A method as claimed in claim 1, in which the sidewalls of the trench are vertical or less than 5° from the vertical.
3. A method as claimed in claim 1 or claim 2, in which the ratio of the depth of the trench to the width of the trench between about 3.5 to 1 and 2.5 to 1.
4. A method as claimed in any preceding claim, in which the depth of the trench is about 3.5 to about 4 microns and the width is about 1 to about 2 microns.
5. A method as claimed in any preceding claim, in which the non-nucleating material comprises silicon dioxide, silicon nitride, or aluminium oxide.
6. A method as claimed in any preceding claim, in which the non-nucleating layer is about 0.2 to about 0.5 nm thick.

7. A method as claimed in any preceding claim, in which the layer of nucleating material is about 300 to about 2500 angstroms thick.
8. A method as claimed in any preceding claim, in which the nucleating material is polycrystalline silicon.
9. A method as claimed in any preceding claim, in which the semiconductor substrate is a silicon substrate.
10. A method as claimed in any preceding claim, in which (Figs 1 to 6) both the side walls and the base of the trench are covered with the non-nucleating material and the layer of nucleating material is provided on the substrate surface into which the trench is let and on the base of the trench, but not on the sidewalls of the trench.
11. A method as claimed in any of claims 1 to 9, in which (Fig 7) the sidewalls but not the base, of the trench are covered with the non-nucleating material and the nucleating material is provided only on the non-nucleating material covering the substrate surface into which the trench is let.
12. A method as claimed in any of claims 1 to 9, in which (Fig 8) the sidewalls, but not the base, of the trench are covered with the non-nucleating material and the nucleating material is provided on the non-nucleating material covering the sidewalls of the trench and the substrate surface into which the trench is let.
13. A method as claimed in any of claims 1 to 9, in which (Fig 9) the sidewalls, but not the base, of the trench are covered with the non-nucleating material and the layer of nucleating material is provided only on the non-nucleating material covering the sidewalls of the trench.

14. A method as claimed in any of claims 1 to 9, in which (Fig 10) both the base and the sidewalls of the trench are covered with the non-nucleating material and the layer of nucleating material is provided over the whole surface of the non-nucleating material.
15. A method as claimed in any of claims 1 to 9, in which (Fig 11) the sidewalls, but not the base, of the trench are covered with the non-nucleating material and the layer of nucleating material is provided over the whole surface of the non-nucleating material and over the exposed substrate base of the trench.
16. A method as claimed in any of claims 1 to 9, in which (Figs 12 and 13) the base, but not the sidewalls, of the trench is covered with the non-nucleating material and the layer of nucleating material is provided on the uncovered substrate sidewalls of the trench and over the whole surface of the non-nucleating material.
17. A method as claimed in any preceding claim, in which the silicon is grown by a gas-solid heterogeneous reaction system.
18. A method as claimed in claim 17, in which the heterogeneous reaction system includes hydrogen, silicon, and chlorine.
19. A method as claimed in claim 18, in which the heterogeneous reaction system is a combination of SiCl_4 and H_2 .
20. A method as claimed in any of claims 17 to 19, in which the silicon is grown at a temperature between about 900 and about 1100°C.
21. A method as claimed in any of claims 17 to 20, in which the silicon is grown in a period of less than about 20 minutes.

22. A method as claimed in any preceding claim, further comprising planarizing the surface of the structure after the silicon has been grown.
23. A method as claimed in claim 22, in which the planarizing is carried out by reactive ion etching.
24. A method as claimed in claim 23, in which the planarizing is carried out employing a gaseous mixture of O_2 and CF_4 .
25. A method as claimed in claim 24, in which the gaseous mixture contains about 20% O_2 and is at a pressure of about 100 millitorr (13.3 N/m^2).

FIG. 1

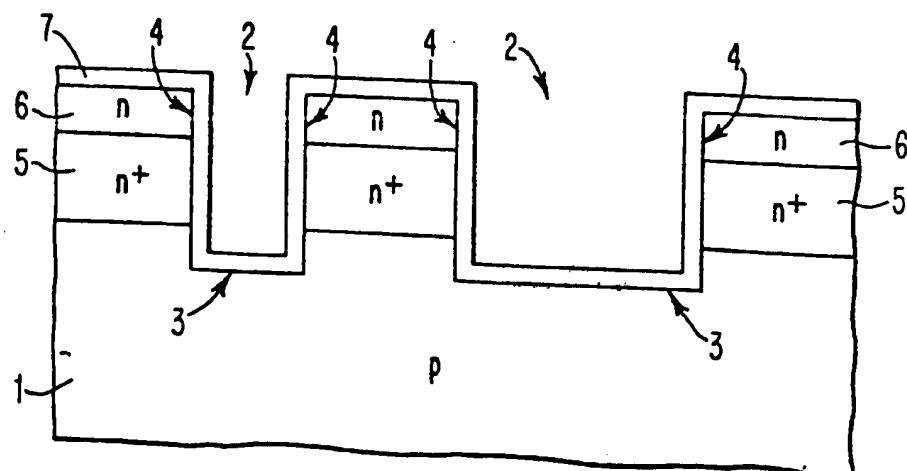


FIG. 2

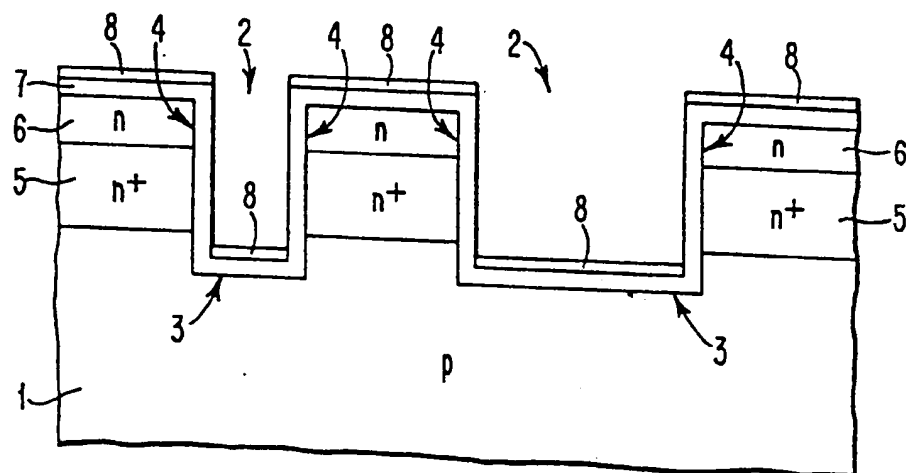


FIG. 3

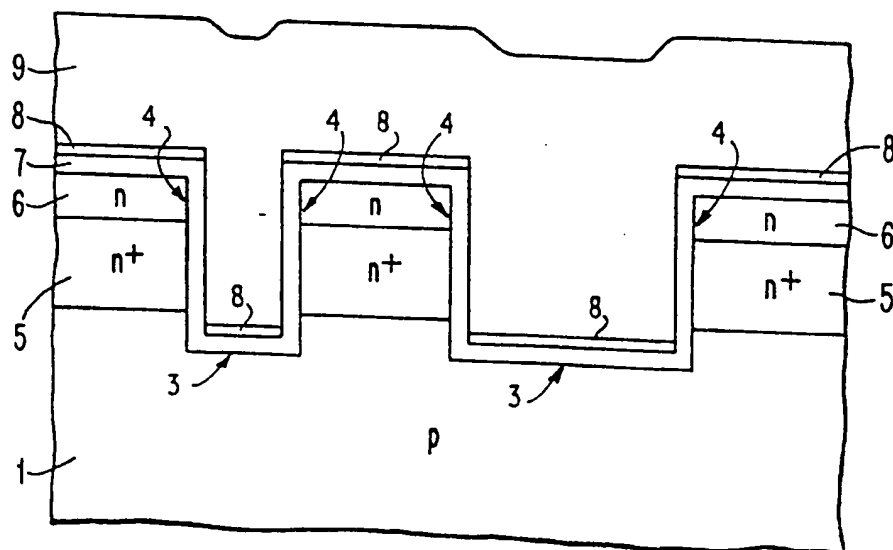


FIG. 4

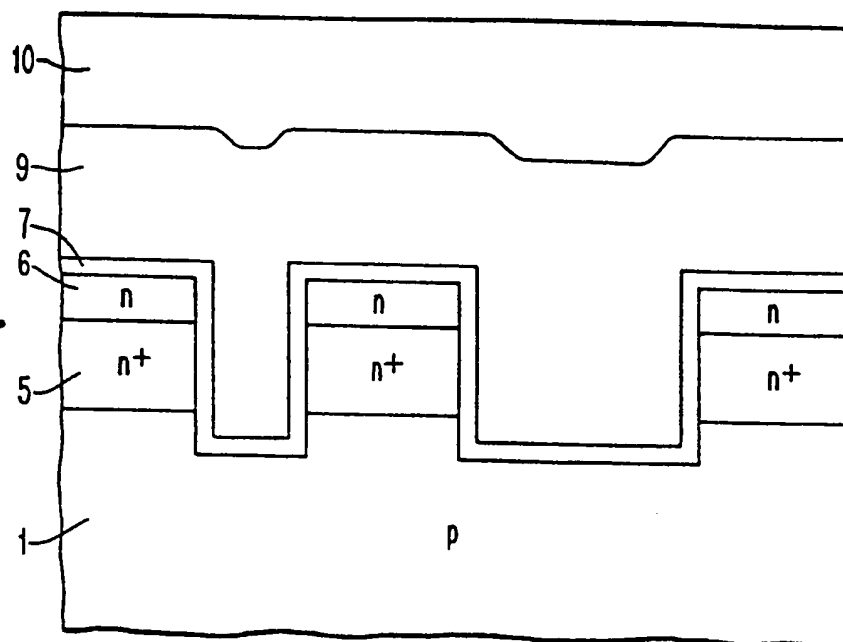


FIG. 5

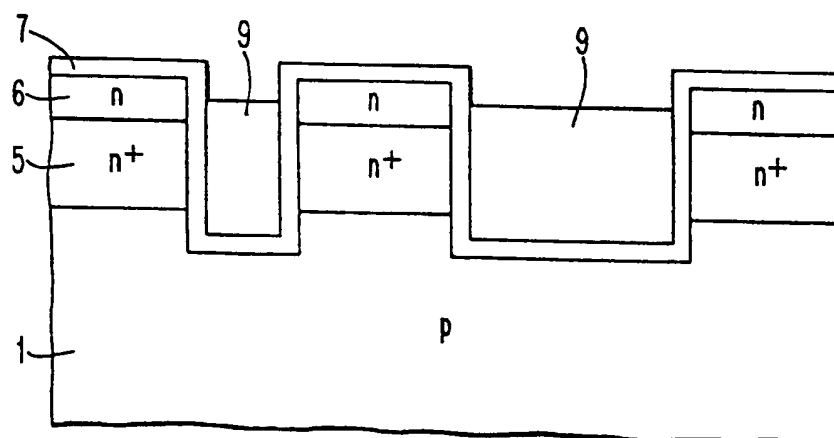
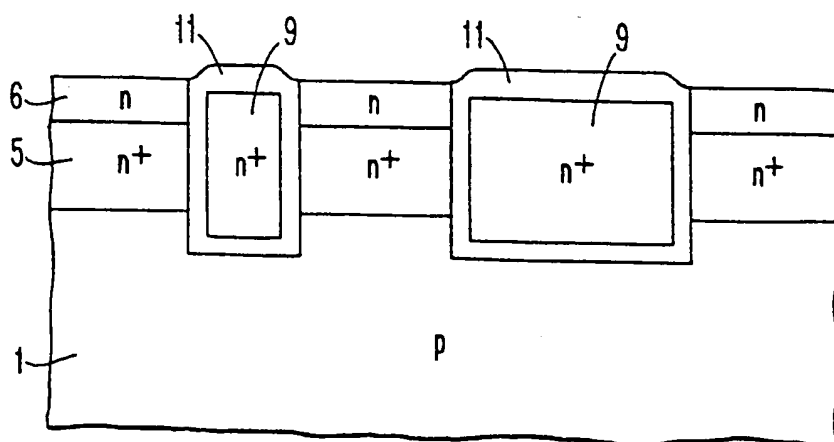


FIG. 6



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FIG. 7

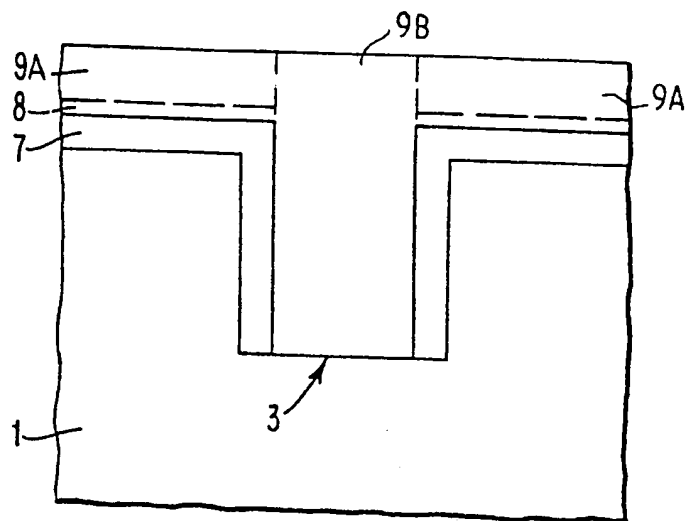


FIG. 8

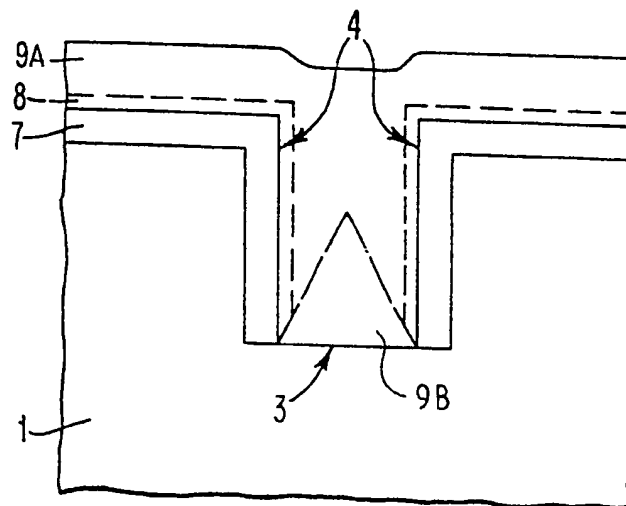


FIG. 9

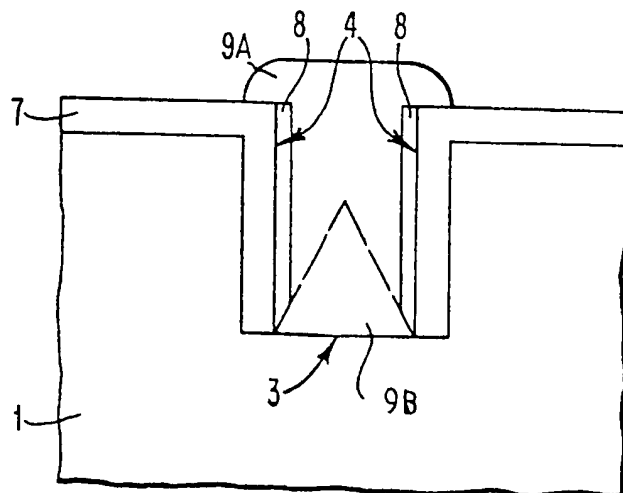


FIG. 10

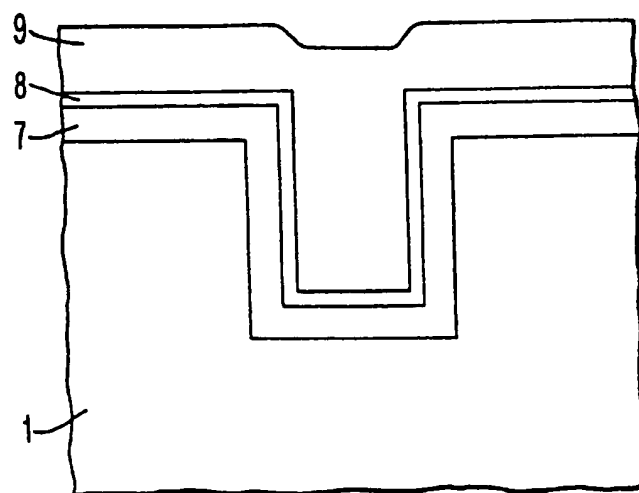


FIG. 11

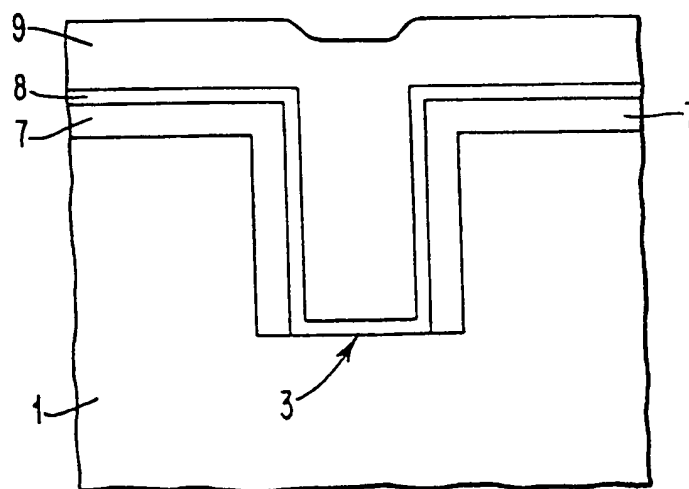


FIG. 12

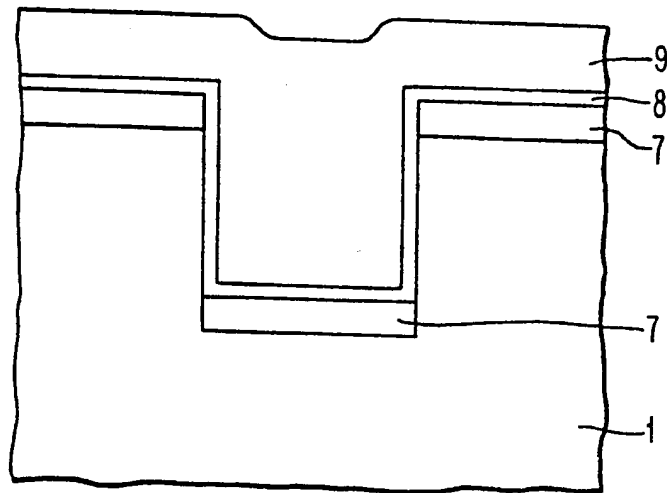


FIG. 13

